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## DESCRIPTION

SUPPORT FOR USE IN CATALYST FOR PRODUCING LOWER ALIPHATIC  
CARBOXYLIC ACID ESTER, CATALYST FOR PRODUCING LOWER  
5 ALIPHATIC CARBOXYLIC ACID ESTER USING THE SUPPORT,  
PROCESS FOR PRODUCING THE CATALYST, AND  
PROCESS FOR PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID  
ESTER USING THE CATALYST.

## 10 Cross-Reference to Related Application

This application is an application filed under 35  
U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.  
§119(e)(1) of the filing date of the Provisional  
Application 60/273,343 filed March 6, 2001, pursuant to  
15 35 §111(b).

## Technical Field

The present invention relates to a support for use  
in a catalyst for producing a lower aliphatic carboxylic  
20 acid ester; a catalyst for producing a lower aliphatic  
carboxylic acid ester using the support; a process for  
producing the catalyst; and a process for producing a  
lower aliphatic carboxylic acid ester using the catalyst.  
More specifically, the present invention relates to a  
25 siliceous support for use in a catalyst for producing a  
lower aliphatic carboxylic acid ester from a lower olefin  
and a lower aliphatic carboxylic acid; a catalyst for  
producing a lower aliphatic carboxylic acid ester using  
the support; a process for producing the catalyst; and a  
30 process for producing a lower aliphatic carboxylic acid  
ester using the catalyst.

## Background Art

As is well known, a corresponding ester can be  
35 produced from a lower aliphatic carboxylic acid and an  
olefin by a gas phase catalytic reaction. Also, a  
catalyst comprising a heteropolyacid and/or a

heteropolyacid salt and supported on a siliceous support is known to be useful in such a reaction. The siliceous support used here is known as a silica support. Specific examples of recent publications disclosing this technique include Japanese Unexamined Patent Publication No. 11-269126 (JP-A-11-269126) and Japanese Unexamined Patent Publication No. 11-263748 (JP-A-11-263748).

JP-A-11-269126 and JP-A-11-263748 disclose a technique of producing a lower aliphatic carboxylic acid ester by contacting a lower aliphatic carboxylic acid and a lower olefin with a heteropolyacid supported on a silica support (siliceous support) in a gas phase. In these patent publications, it is stated that, to achieve optimal performance, the silica support preferably has a purity of 99% by weight or more, because impurities may adversely affect the catalytic activity. As such, the siliceous support used as a support for improving the catalytic activity preferably has a high silicon purity. However, siliceous supports having a high silicon purity suffer from a very low strength and if a catalyst using such a support having a low strength is used, cracking may be generated at the preparation of the catalyst, or cracking or abrasion of the catalyst may be generated according to the amount of use in the production of esters, giving rise to an increase in the pressure loss of a reactor and, in turn, to failure of safe operation.

#### Disclosure of Invention

The object of the present invention is to provide a support capable of providing a stably operable catalyst, for producing a lower aliphatic carboxylic acid ester, which prevents a great reduction in the catalytic activity and protects the catalyst from cracking or abrasion during the production of a lower aliphatic carboxylic acid ester, wherein the catalyst is supported on a siliceous support and used in the production of a lower aliphatic carboxylic acid ester from a lower olefin

and a lower aliphatic carboxylic acid. The object of the present invention includes providing a catalyst for producing a lower aliphatic carboxylic acid ester using the support, a process for producing the catalyst and a process for producing a lower aliphatic carboxylic acid ester using the catalyst.

To attain the above-described objects, the present invention provides a siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 39.7 to 46.3% by mass.

The present invention also provides a siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

The present invention also provides a siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a crush strength of 30 N or more.

The present invention also provides a catalyst supported on a support, which is a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, wherein the support is any one of the above-described supports of the present invention.

The present invention also provides a process for producing a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, the process comprising a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on any one of the above-described supports of the present invention.

The present invention also provides a process for producing a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, the  
5 process comprising the following first and second steps:

First Step:

a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on any one of the above-described supports of the present  
10 invention to obtain a heteropolyacid and/or heteropolyacid salt-supported catalyst;

Second Step:

a step of contacting the heteropolyacid and/or heteropolyacid salt-supported catalyst obtained in the  
15 first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for producing a lower aliphatic carboxylic acid ester.

20 The present invention also provides a process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the above-described catalyst for producing a lower aliphatic  
25 carboxylic acid ester of the present invention.

Brief Description of Drawings

Fig. 1 is a graph showing the crush strength and the specific activity with respect to the silica content of  
30 the support in catalysts used in Examples of the present invention and Comparative Examples.

Best Mode for Carrying Out the Invention

The present inventors have made extensive  
35 investigations for a catalyst supported on a siliceous support and used in the production of a lower aliphatic carboxylic acid ester from a lower olefin and a lower



The heteropolyacids which can be used in the

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMO_{12}O_{40}] \cdot xH_2O$

Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdosilicic acid	$H_{4+n}[SiV_nMo_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_4[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_3[PMo_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of 1 or more. However, the present invention is by no means limited thereto.

Among these, preferred are tungstosilicic acid,  
 5 tungstophosphoric acid, molybdo-phosphoric acid,  
 molybdosilicic acid, vanadotungstosilicic acid and  
 vanadotungstophosphoric acid, more preferred are  
 tungstosilicic acid, tungstophosphoric acid,  
 vanadotungstosilicic acid and vanadotungstophosphoric  
 10 acid.

The synthesis method for these heteropolyacids is not particularly limited and any method may be used. For example, the heteropolyacid may be obtained by heating an acidic aqueous solution containing a salt of molybdic  
 15 acid or tungstic acid and a simple oxygen acid of hetero atom or a salt thereof (pH: about 1 to 2). For isolating the heteropolyacid compound from the aqueous heteropolyacid solution produced, a method of crystallizing and separating the compound in the form of  
 20 a metal salt may be used. Specific examples thereof include those described in Shin Jikken Kagaku Koza 8, Muki Kagoubutsu no Gosei (III) (New Experimental Chemistry Course 8, Synthesis of Inorganic Compounds (III)), 3rd ed., page 1413, edited by Nippon Kagaku Kai, published by Maruzen on August 20, 1984, however, the  
 25 present invention is not limited thereto. The Keggin structure of the heteropolyacid synthesized may be identified by the chemical analysis or by the X-ray diffraction or UV or IR measurement.



Examples of the starting material for the element of forming a heteropolyacid salt include lithium nitrate, lithium acetate, lithium sulfate, lithium sulfite, lithium carbonate, lithium phosphate, lithium oxalate,

lithium nitrite, lithium chloride, lithium citrate,  
sodium nitrate, sodium acetate, sodium sulfate, sodium  
carbonate, monosodium phosphate, disodium phosphate,  
sodium oxalate, sodium nitrite, sodium chloride, sodium  
5 citrate, magnesium nitrate hexahydrate, magnesium acetate  
tetrahydrate, magnesium sulfate, magnesium carbonate,  
magnesium phosphate tricosahydrate, magnesium oxalate  
dihydrate, magnesium chloride, magnesium citrate, barium  
nitrate, barium acetate, barium sulfate, barium  
10 carbonate, barium hydrogenphosphate, barium oxalate  
monohydrate, barium sulfite, barium chloride, barium  
citrate, copper nitrate, copper acetate, copper sulfate,  
copper carbonate, copper diphosphate, copper oxalate,  
copper chloride, copper citrate, aurous chloride,  
15 chloroauric acid, auric oxide, auric hydroxide, auric  
sulfide, aurous sulfide, gallium dichloride, gallium  
monochloride, gallium citrate, gallium acetate, gallium  
nitrate, gallium sulfate, gallium phosphate, ammonium  
acetate, ammonium carbonate, ammonium nitrate, ammonium  
20 dihydrogenphosphate, ammonium hydrogencarbonate, ammonium  
citrate, ammonium nitrate, diammonium phosphate,  
monoammonium phosphate and ammonium sulfate, however, the  
present invention is by no means limited thereto.

Among these, preferred are lithium nitrate, lithium  
25 acetate, lithium carbonate, lithium oxalate, lithium  
citrate, sodium nitrate, sodium acetate, sodium  
carbonate, sodium oxalate, sodium citrate, copper  
nitrate, copper acetate, copper carbonate, copper  
citrate, aurous chloride, chloroauric acid, gallium  
30 citrate, gallium acetate and gallium nitrate, and more  
preferred are lithium nitrate, lithium acetate, lithium  
carbonate, lithium oxalate, lithium citrate, sodium  
nitrate, sodium acetate, sodium carbonate, sodium  
oxalate, sodium citrate, copper nitrate, copper acetate,  
35 copper carbonate and copper citrate.

Specific examples of the heteropolyacid salts  
include lithium salt of tungstosilicic acid, sodium salt

of tungstosilicic acid, copper salt of tungstosilicic acid, gold salt of tungstosilicic acid, gallium salt of tungstosilicic acid, lithium salt of tungstophosphoric acid, sodium salt of tungstophosphoric acid, copper salt of tungstophosphoric acid, gold salt of tungstophosphoric acid, gallium salt of tungstophosphoric acid, lithium salt of molybdophosphoric acid, sodium salt of molybdophosphoric acid, copper salt of molybdophosphoric acid, gold salt of molybdophosphoric acid, gallium salt of molybdophosphoric acid, lithium salt of molybdosilicic acid, sodium salt of molybdosilicic acid, copper salt of molybdosilicic acid, gold salt of molybdosilicic acid, gallium salt of molybdosilicic acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid, gallium salt of vanadotungstophosphoric acid, lithium salt of vanadomolybdophosphoric acid, sodium salt of vanadomolybdophosphoric acid, copper salt of vanadomolybdophosphoric acid, gold salt of vanadomolybdophosphoric acid, gallium salt of vanadomolybdophosphoric acid, lithium salt of vanadomolybdosilicic acid, sodium salt of vanadomolybdosilicic acid, copper salt of vanadomolybdosilicic acid, gold salt of vanadomolybdosilicic acid and gallium salt of vanadomolybdosilicic acid.

Among these, preferred are lithium salt of tungstosilicic acid, sodium salt of tungstosilicic acid, copper salt of tungstosilicic acid, gold salt of tungstosilicic acid, gallium salt of tungstosilicic acid, lithium salt of tungstophosphoric acid, sodium salt of tungstophosphoric acid, copper salt of tungstophosphoric

acid, gold salt of tungstophosphoric acid, gallium salt of tungstophosphoric acid, lithium salt of molybdophosphoric acid, sodium salt of molybdophosphoric acid, copper salt of molybdophosphoric acid, gold salt of molybdophosphoric acid, gallium salt of molybdophosphoric acid, lithium salt of molybdosilicic acid, sodium salt of molybdosilicic acid, copper salt of molybdosilicic acid, gold salt of molybdosilicic acid, gallium salt of molybdosilicic acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid and gallium salt of vanadotungstophosphoric acid.

More preferred are lithium salt of tungstosilicic acid, sodium salt of tungstosilicic acid, copper salt of tungstosilicic acid, gold salt of tungstosilicic acid, gallium salt of tungstosilicic acid, lithium salt of tungstophosphoric acid, sodium salt of tungstophosphoric acid, copper salt of tungstophosphoric acid, gold salt of tungstophosphoric acid, gallium salt of tungstophosphoric acid, lithium salt of vanadotungstosilicic acid, sodium salt of vanadotungstosilicic acid, copper salt of vanadotungstosilicic acid, gold salt of vanadotungstosilicic acid, gallium salt of vanadotungstosilicic acid, lithium salt of vanadotungstophosphoric acid, sodium salt of vanadotungstophosphoric acid, copper salt of vanadotungstophosphoric acid, gold salt of vanadotungstophosphoric acid and gallium salt of vanadotungstophosphoric acid.

35           The method for loading a heteropolyacid salt on a support roughly includes the following three methods (1) to (3):

(1) a method of loading a desired heteropolyacid on a support and then loading a starting material for the desired element for forming a salt,

5 (2) a method of loading a desired heteropolyacid and a starting material for the element of forming a salt, together on a support or loading a previously prepared heteropolyacid salt, and

10 (3) a method of previously loading a starting material for the element for forming a salt on a support and then loading a desired heteropolyacid.

In any of these methods (1) to (3), the heteropolyacid, a salt thereof and the starting material for the element of forming a salt each can be loaded on a support after dissolving it or suspending it in an  
15 appropriate solvent. The solvent may be any solvent as long as it can uniformly dissolve or suspend the desired heteropolyacid, a salt thereof and the starting material for the element of forming a salt, and examples of the solvent which can be used include water, an organic  
20 solvent and a mixture thereof. Among these, preferred are water, alcohol and carboxylic acid.

The method for dissolving or suspending the desired heteropolyacid, a salt thereof and the starting material for the element of forming a salt may also be any method  
25 as long as it can uniformly dissolve or suspend the materials. In the case of a free acid, a free acid which can dissolve may be dissolved as it is in a solvent and even in the case of a free acid which cannot completely dissolve, if the free acid can be uniformly suspended by  
30 forming it into fine powder, the free acid may be suspended as such.

In the method (1), a solution or suspension obtained by dissolving or suspending a heteropolyacid in a solvent is absorbed into a support to thereby load the  
35 heteropolyacid on the support and then, a solution or suspension of a starting material for the element of forming a desired salt is absorbed into the support to

thereby load the element. At this time, a neutralization reaction proceeds on the support and, as a result, a catalyst having supported thereon a heteropolyacid salt can be prepared.

5           In the method (2), a heteropolyacid and a starting  
material for the element of forming a salt are dissolved  
or suspended together or these are dissolved or suspended  
separately and then mixed, and the thus-prepared solution  
or suspension is absorbed into a support and thereby  
10       loaded on the support. If the compound is in the state  
of a heteropolyacid salt, a uniform solution or  
suspension may be obtained in the same manner as in the  
case of a free acid.

In the method (3), a solution or suspension of a starting material for the element of forming a salt is previously prepared, the solution or suspension is absorbed into a support to thereby load the element, and then a desired heteropolyacid is loaded thereon. This method includes a method of using an element which is previously contained in the support and can form a heteropolyacid salt.

More specifically, a part or all of the elements previously contained in a support sometimes act to form a salt of a heteropolyacid on loading and, as a result, a heteropolyacid salt is formed. Examples of such an element include potassium, sodium, calcium, iron, magnesium, titanium and aluminum, however, the present invention is not limited thereto.

The kind of the element previously contained in a support and the amount thereof can be measured by chemical analysis such as ICP, fluorescent X-ray spectrometry and atomic absorption spectrometry. The kind and the amount of the element vary depending on the support, however, potassium, sodium, calcium, iron, magnesium, titanium and ammonium are sometimes contained in a relatively large amount and the content thereof is approximately from 0.001 to 5.0% by mass. Therefore,

depending on the combination of a support and a heteropolyacid, the element may be previously contained in the support in an amount large enough to form a salt, though this may vary depending on the kind and the amount  
5 of the heteropolyacid supported.

The amount of a heteropolyacid salt supported is preferably from 10 to 150% by mass, more preferably from 30 to 100% by mass, based on the total weight of the support. If the heteropolyacid salt content is less than  
10 10% by mass, the active component content of the catalyst is too small and the activity per unit weight of catalyst may disadvantageously decrease. If the heteropolyacid salt content exceeds 150% by mass, the effective pore volume decreases and, as a result, the effect of the  
15 increase in the supported amount may not be brought out and, at the same time, coking is disadvantageously liable to occur to seriously shorten the catalyst life.

The method for loading a solution or suspension of a heteropolyacid and/or a heteropolyacid salt on a support  
20 is not particularly limited and a known method may be used. More specifically, for example, the catalyst may be prepared by dissolving a heteropolyacid in distilled water corresponding to the liquid absorption amount of a support used and impregnating the solution into the  
25 support. Also, the catalyst may be prepared by using an excess aqueous solution, dipping a support in the heteropolyacid solution while appropriately moving the support and then removing the excess acid through filtration. The volume of the solution or suspension  
30 used at this time varies depending on the support or loading method used.

The thus-obtained wet catalyst is suitably dried by placing it in a heating oven for a few hours. The drying method is not particularly limited and any method such as  
35 standing or belt conveyor may be used. After the drying, the catalyst is cooled to the ambient temperature in a desiccator so as not to absorb moisture.

The amount of a heteropolyacid and/or a heteropolyacid salt supported in the thus-obtained heteropolyacid salt supported catalyst can be simply calculated by subtracting the weight of the support used from the weight after drying of the catalyst prepared. To be more exact, the supported amount can be determined by chemical analysis such as ICP, fluorescent X-ray spectrometry and atomic absorption spectrometry.

The catalyst for producing a lower aliphatic carboxylic acid ester of the present invention is preferably produced by a production process comprising a first step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support of the present invention to obtain a catalyst, and a second step of contacting this catalyst with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for the production of a lower aliphatic carboxylic acid ester.

In this method, the loading of a heteropolyacid and/or a heteropolyacid salt on a support in the first step can be performed according to the method described in detail above.

The second step in the above-described production process is a step of contacting the catalyst having supported thereon a heteropolyacid and/or a heteropolyacid salt, which is obtained in the first step, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols.

The method for contacting the supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is not particularly limited and, for example, the following methods may be used:



In view of the time period necessary for re-filling the catalyst or the vessel cost, the preferred embodiment of the second step includes a method of filling the catalyst obtained in the first step into a reactor which is used at the time of reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, and then contacting therewith a gas containing at least one member

selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols before feeding the reaction starting materials. This method may be performed in either a closed circulatory system or a flow system.

The second step is preferably performed under a condition higher than the dew point of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols. If the condition is less than the dew point of this gas, a part of the gas may turn into a liquid. In this case, a heteropolyacid and/or a heteropolyacid salt supported on the catalyst in the first step, or other catalyst components supported if desired, may dissolve out to change the catalyst composition and in the worst case, the catalyst may be deactivated. Insofar as the catalyst is not adversely affected, the conditions in performing the second step are not particularly limited.

The preferred embodiment of a condition higher than the dew point of the above-described gas may vary depending on the composition of the gas or the pressure or the like in the practice, however, the contact temperature is preferably from 80 to 300°C, more preferably from 100 to 260°C.

The contact pressure is not particularly limited and may be either normal pressure or an applied pressure. The contact pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The lower aliphatic carboxylic acid in the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic carboxylic acid having from 1 to 6 carbon atoms. Specific examples thereof include formic acid, acetic acid, propionic acid, n-butyric acid

and isobutyric acid. Among these, preferred are acetic acid and propionic acid.

The lower aliphatic alcohol in the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is preferably a lower aliphatic alcohol having from 1 to 6 carbon atoms. Specific examples thereof include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol. Among these, particularly preferred are methanol, ethanol and n-propanol.

The composition of the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is not particularly limited, and water, a lower aliphatic carboxylic acid and/or a lower aliphatic alcohol can be mixed at an arbitrary ratio. The composition is preferably such that water : lower aliphatic carboxylic acid : lower aliphatic alcohol = 1.0 : 0.1 to 10.0 : 0.1 to 5.0 in terms of the molar ratio. The composition of the gas may be constant from the beginning to the end of contacting or may be changed according to the contact time or the stage of contacting.

The gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is more preferably water alone or a mixed gas of water and acetic acid, still more preferably a mixed gas of water and acetic acid, because a predetermined effect can be obtained within a short period of time. In the case of using a mixed gas of water and acetic acid, the composition thereof is not particularly limited but preferably such that water : acetic acid = 1.0 : 0.1 to 10.0, more preferably water : acetic acid = 1.0 : 0.5 to 5.0, in terms of the molar ratio.

The gas hourly space velocity (GHSV) of the gas, which is the speed of feeding the gas in performing the

contact with a gas containing at least one member  
selected from the group consisting of water, lower  
aliphatic carboxylic acids and lower aliphatic alcohols  
in the second step, is not particularly limited. The  
5 GHSV is preferably from 100 to 7,000  $\text{hr}^{-1}$ , more  
preferably from 300 to 3,000  $\text{hr}^{-1}$ . If the GHSV is too  
high, the amount of the gas used increases and this is  
not preferred in view of the cost. From this standpoint,  
the contacting may also be performed in the state such  
10 that the gas is fed in a constant amount and enclosed in  
a vessel.

The contact time is not particularly limited but  
preferably from 0.5 to 200 hours, more preferably from  
0.5 to 100 hours, and most preferably from 0.5 to 50  
15 hours. The optimal contact time varies depending on the  
composition and concentration of the gas, the temperature  
and pressure at the contacting, and the catalyst  
components.

Generally, if the contact time is less than 0.5  
20 hours, the effect of the second step may not be fully  
brought out, whereas if the contact time is prolonged,  
the effect is liable to increase, however, even if the  
contact time is prolonged to exceed 200 hours, the effect  
does not increase any more and, moreover, in the case  
25 where gas is contacted in the flowing state, the amount  
of the gas used increases and this is not preferred in  
view of the profitability.

These first and second steps may be performed either  
continuously or completely independently of each other.  
30 More specifically, for example, after purchasing the  
catalyst passed through the first step, the second step  
may be performed using this catalyst.

Furthermore, in the process for producing the  
catalyst for producing a lower aliphatic carboxylic acid  
35 ester according to the present invention, other steps may  
be provided, if desired. Such a step may be performed  
before, after or during the loading of a heteropolyacid

The lower aliphatic carboxylic acid is suitably a carboxylic acid having from 1 to 4 carbon atoms and specific examples thereof include formic acid, acetic acid, propionic acid, butyric acid, acrylic acid and methacrylic acid.

The proportion between the lower olefin and the lower aliphatic carboxylic acid used as the starting materials is not particularly limited. In view of the conversion of the lower olefin, the lower olefin is preferably used in an equimolar or excess molar amount to the lower aliphatic carboxylic acid. To speak specifically, the molar ratio of the lower olefin to the lower aliphatic carboxylic acid is preferably in the range of lower olefin : lower aliphatic carboxylic acid = from 1:1 to 30:1, more preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

In the process for producing a lower aliphatic carboxylic acid ester of the present invention, a slight amount of water is preferably added to the starting materials comprising a lower olefin and a lower aliphatic carboxylic acid from the standpoint of maintaining the catalytic activity. However, if an excessively large amount of water is added, the amount of by-products such as alcohol and ether disadvantageously increases. The amount of water added is preferably, in terms of the molar ratio of water to the sum total of lower olefin and lower aliphatic monocarboxylic acid as starting materials and water added, from 0.5 to 15 mol%, more preferably from 2 to 8 mol%.

In this process, preferred reaction conditions such as temperature and pressure vary depending on the kinds of the lower olefin and lower aliphatic carboxylic acid used as the starting materials. The reaction conditions such as temperature and pressure are preferably combined so that the starting materials can each be kept in the gas state and the reaction can satisfactorily proceed. In general, the temperature is preferably from 120 to 300°C, more preferably from 140 to 250°C. The pressure is preferably from 0 to 3 MPaG (gauge pressure), more preferably from 0 to 2 MPaG (gauge pressure).

The each starting material is not particularly limited regarding the GHSV, however, if the GHSV is

excessively high, the starting materials pass through before the reaction satisfactorily proceeds, whereas if it is too low, there may arise problems such as reduction in the productivity. The GHSV is preferably from 100 to 7,000  $\text{hr}^{-1}$ , more preferably from 300 to 3,000  $\text{hr}^{-1}$ .

The unreacted lower olefin, and also the alcohol and the ether as by-products in the reaction may be recycled and used as they are. At this time, substances harmful to the catalyst for the production of a lower aliphatic carboxylic acid ester, such as butene and aldehyde, are difficult to separate from olefin, alcohol, ether and the like and may be sent to the reactor. If this is so, the catalyst performance may be seriously reduced or the life thereof may be extremely shortened. Accordingly, a catalyst, for producing a lower aliphatic carboxylic acid ester of the present invention, and which can greatly reduce the production of these by-products at the reaction stage, is used. The process for producing a lower aliphatic carboxylic acid ester of the present invention is effective particularly when the above-described recycling system is included in the production process.

The present invention will be further illustrated below by referring to the Examples and Comparative Examples, however, these examples are described to show the outline of the present invention and the present invention should not be construed as being limited thereto.

In the examples, the measured values were obtained by analysis or measurement performed according to the following methods.

Analysis Method of Contents of Silicon and Other Elements in Support:

A support was weighed to 1 g and 10 ml of 50% HF (aqueous hydrofluoric acid solution) was added. In this liquid, a sample was dissolved. When an undissolved portion was present, a pressure acidolysis was further

Specific surface area: 110.8 m<sup>2</sup>/g



Pore volume: 0.42 cm<sup>3</sup>/g

Crush strength: 84 N

Support 3:

Natural silica (KA-160, produced by SUD-CHEMIE  
CATALYSTS JAPAN, INC.)

Specific surface area: 158.1 m<sup>2</sup>/g

Pore volume: 0.42 cm<sup>3</sup>/g

Crush strength: 71 N

Support 4:

Synthetic silica (N602T, produced by NIKKI CHEMICAL  
CO., LTD.)

Specific surface area: 132 m<sup>2</sup>/g

Pore volume: 0.7 cm<sup>3</sup>/g

Crush strength: 30 N

Support 5:

Synthetic silica (CARIACT Q-10, produced by FUJI  
SILYSIA CHEMICAL LTD.)

Specific surface area: 309 m<sup>2</sup>/g

Pore volume: 1.02 cm<sup>3</sup>/g

Crush strength: 20 N

Support 6:

Synthetic silica (Grace 57, produced by Grace  
Devison K.K.)

Specific surface area: 430 m<sup>2</sup>/g

Pore volume: 1.0 cm<sup>3</sup>/g

Crush strength: 13 N

Support 7:

Silica-alumina (N631L, produced by NIKKI CHEMICAL  
CO., LTD.)

Specific surface area: 480 m<sup>2</sup>/g

Pore volume: 0.18 cm<sup>3</sup>/g

Crush strength: 1900 N

These supports each was analyzed on the contents of  
elements. The obtained content as an oxide of each  
element is shown in Table 1.

Furthermore, the crack ratio of each support is  
shown in Table 2.

Table 1

	SiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Others
Support 1	96.04	0.657	1.389	0.229	0.762	0.928
Support 2	93.11	0.843	1.587	0.356	1.923	2.185
Support 3	95.60	0.778	1.046	0.132	0.698	1.750
Support 4	98.44	0.502	0.423	0.120	0.275	0.236
Support 5	99.54	0.172	0.077	0.045	0.027	0.140
Support 6	99.71	0.105	0.105	0.049	0.032	0.002
Support 7	81.60	0.256	0.018	0.042	12.600	5.480

unit: wt%

Table 2

	Crack Ratio (%)
Support 1	<1.0
Support 2	<1.0
Support 3	<1.0
Support 4	<1.0
Support 5	10.0
Support 6	15.0
Support 7	<1.0

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#### Production Operation of Catalyst:

Using each of those supports, catalysts were produced as follows.

Supports 1 to 7 were each preliminarily dried for 4 hours in a (hot-air type) drier previously adjusted to 110°C. After the preliminary drying, each support was measured for the bulk density using a 1 liter measuring cylinder. A predetermined amount of tungstosilicic acid was weighed and after adding thereto 15 ml of distilled water, uniformly dissolved. Furthermore, distilled water was added to make an amount described in the column of Prepared Liquid Volume of Table 3. Thereafter, the preliminarily dried support was weighed to a weight described in the column of Support Weight of Table 3, added to the impregnating solution and impregnated therewith while thoroughly stirring. The support impregnated with the solution was transferred to a porcelain dish, air-dried for 1 hour and then dried in a hot-air type drier adjusted to 150°C for 5 hours. After the drying, the catalyst was transferred to a desiccator

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and allowed to cool to room temperature. The thus-obtained catalyst was weighed. Further, the crush strength and crack ratio were measured.

The obtained characteristic data of each catalyst  
5 are shown in Table 3.

Table 3

Catalyst No.	Support No.	Bulk Density of Support (g/L)	Weight of Support (g)	Catalyst Component	Amount of Catalyst Component Supported (g/L)	Prepared Liquid Volume (ml)	Dry Weight (g)	Crush Strength (N)	Crack Ratio (%)
1	1	558	55.8	$\text{Li}_{0.01}\text{H}_{3.99}\text{SiW}_{12}\text{O}_{40}$	300	34	86.2	60	<1.0
2	1	558	55.8	$\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	550	34	110.5	66	<1.0
3	2	573	57.3	$\text{Li}_{0.01}\text{H}_{3.99}\text{SiW}_{12}\text{O}_{40}$	300	33	87.1	81	<1.0
4	3	575	57.5	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	300	33	87.9	70	<1.0
5	3	575	57.5	$\text{Li}_{0.001}\text{H}_{2.999}\text{PW}_{12}\text{O}_{40}$	300	34	88.1	69	<1.0
6	4	448	44.8	$\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	400	41	85.2	28	<1.0
7	5	456	45.6	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	300	43	75.9	16	8.2
8	5	456	45.6	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	350	43	80.9	17	8.9
9	6	413	41.3	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	300	50	71.0	12	14.2
10	6	413	41.3	$\text{Li}_{0.1}\text{H}_{3.9}\text{SiW}_{12}\text{O}_{40}$	350	50	76.2	11	15.6
11	7	607	60.7	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	300	33	90.5	1800	<1.0

15           The results obtained are shown in Tables 4 and 5.

Table 4

Example No.	Catalyst No.	Pre-Treatment Conditions				Ethyl Acetate Production Conditions				Reaction Results			
		Treated Gas Composition HOAc:H <sub>2</sub> O	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Time (hr)	Composition of Starting Gases C <sub>2</sub> H <sub>4</sub> :HOAc:H <sub>2</sub> O:N <sub>2</sub>	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temperature (°C)	Reaction Time (hr)	Ethyl Acetate STY (g/L·hr)	Selectivity of Butene (%)
1	1	none	-	-	-	-	78.5:8:4.5:9	60	0.8	165	5	181	0.01
2	2	none	-	-	-	-	70:8:4:18	60	0.6	165	5	186	1.97
3	3	none	-	-	-	-	70:8:4:18	40	1.0	165	5	184	0.21
4	4	none	-	-	-	-	70:8:4:18	80	0.8	165	5	187	1.19
5	5	none	-	-	-	-	78.5:8:4.5:9	60	0.6	165	5	174	1.27
6	6	none	-	-	-	-	70:8:3:19	60	0.8	170	5	190	2.34
7	2	6:6	60	0.8	165	12	78.5:8:4.5:9	60	0.8	165	5	208	0.22
8	5	6:6	60	0	165	12	78.5:8:4.5:9	60	0.8	165	5	205	0.26

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Analysis Method for Condensed Solution:

An analysis solution was prepared by adding 1 ml of 1,4-dioxane as the internal standard to 10 ml of the reaction solution, 0.4  $\mu$ l of the analysis solution was injected, and the analysis was performed using the internal standard method under the following conditions. Gas chromatography:

GC-14B, manufactured by Shimadzu Corporation  
Column:

capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25  $\mu$ m)

Carrier gas:

nitrogen (split ratio: 20, column flow rate: 1 ml/min)

Temperature conditions:

The detector and the vaporization chamber were at a temperature of 200°C and the column temperature was kept at 40°C for 7 minutes from the initiation of analysis, thereafter elevated up to 230°C at a temperature rising rate of 10°C/min, and kept at 230°C for 5 minutes.

Detector:

FID ( $H_2$  pressure: 70 KPa, air pressure: 100 KPa)

Analysis Method for Uncondensed Gas:

Using an absolute calibration curve method, the analysis was performed under the following conditions by sampling 50 ml of the effluent gas and passing the whole amount thereof into a 1 ml-volume gas sampler attached to the gas chromatograph.

1. Ether, Carboxylic Acid Ester, Alcohol and Trace By-Products

Gas chromatograph:

gas chromatograph (GC-14, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)



Column: packed column SPAN 80, 15% Shinchrom A of 60 to 80 mesh (length: 5 m)  
 Carrier gas: nitrogen (flow rate: 25 ml/min)  
 Temperature conditions:  
 the detector and the vaporization chamber were at a temperature of 120°C, and the column temperature was 65°C and constant.  
 Detector: FID (H<sub>2</sub> pressure: 60 KPa, air pressure: 100 KPa)

## 2. Butene:

### Gas chromatograph:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unicarbon A-400 of 80/100 mesh, length: 2 m

Carrier gas: helium (flow rate: 23 ml/min)

### Temperature conditions:

the detector and the vaporization chamber were at a temperature of 130°C, and the column temperature was elevated from 40°C to 95°C at a temperature rising rate of 40°C/min.

Detector: FID (H<sub>2</sub> pressure: 70 KPa, air pressure: 100 KPa)

## 3. Ethylene:

### Gas chromatograph:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler for Shimadzu gas chromatograph (MGS-4, measuring tube: 1 ml)

Column: packed column Unibeads IS, length: 3 m

Carrier gas: helium (flow rate: 20 ml/min)

### Temperature conditions:

the detector and the vaporization chamber

were at a temperature of 120°C, and the column temperature was 65°C and constant.  
 Detector: TCD (He pressure: 70 KPa, current: 90 mA, temperature: 120°C)

Fig. 1 is a graph where based on the results above, the crush strength (N) of the catalyst support and the specific activity of the catalyst are plotted with respect to the silica content (wt%). It is seen from Fig. 1 that when the silicon content of the siliceous support according to the present invention is in the range of 85 to 99% by mass in terms of silica, the obtained catalyst can have high strength and high activity.

#### Industrial Applicability

According to the present invention, at the time of producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic monocarboxylic acid in a gas phase, a catalyst having a silicon content in a predetermined range is used as the siliceous support of the catalyst for the production, whereby a catalyst having predetermined strength and exhibiting performances of a predetermined level can be obtained and the production operation can be stably performed without causing cracking or abrasion of the catalyst even in long-term use.